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Anisotropic reversed micelles with fluorocarbon-hydrocarbon hybrid surfactants in supercritical CO₂

Masanobu Sagisaka^{a,}, Shinji Ono^a, Craig James^a, Atsushi Yoshizawa^a, Azmi Mohamed^{b,c}, Frédéric Guittard^d, Robert M. Enick^e, Sarah E. Rogers^f, Adam Czajka^g, Christopher Hill^g, and Julian Eastoe^{g,*}*

^a Department of Frontier Materials Chemistry, Graduate School of Science and Technology, Hirosaki University,
3 Bunkyo-cho, Hirosaki, Aomori 036-8561, JAPAN

^b Department of Chemistry, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris,
35900 Tanjong Malim, Perak, Malaysia

^c Nanotechnology Research Centre, Faculty of Science and Mathematics, Universiti Pendidikan Sultan
Idris, 35900 Tanjong Malim, Perak, Malaysia

^d Univ. Cote d'Azur, NICE-Lab, 61-63 av. S. Viel, 06200 Nice, France

^e Department of Chemical and Petroleum Engineering, University of Pittsburgh, 940 Benedum Hall,
3700 O'Hara Street, Pittsburgh, Pennsylvania 15261, United States

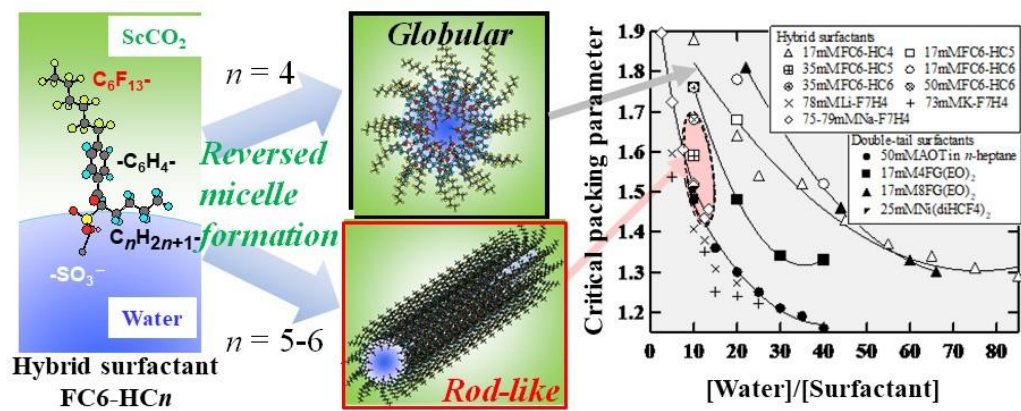
^f ISIS-CCLRC, Rutherford Appleton Laboratory, Chilton, Oxon OX11 0QX, U.K.

^g School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, U.K.

*Corresponding authors

E-mail addresses: sagisaka@hirosaki-u.ac.jp (M. Sagisaka), Julian.Eastoe@bristol.ac.uk (J. Eastoe)

20 Previous work (M. Sagisaka, et al. *Langmuir* 31 (2015) 7479-7487), showed the most effective
21 fluorocarbon (FC) and hydrocarbon (HC) chain lengths in the hybrid surfactants FC m -HC n (sodium 1-
22 oxo-1-[4-(perfluoroalkyl)phenyl]alkane-2-sulfonates, where m = FC length and n = HC length) were m
23 and n = 6 and 4 for water solubilization, whereas m 6 and n 6, or m 6 and n 5, were optimal chain lengths
24 for reversed micelle elongation in supercritical CO₂. To clarify why this difference of only a few
25 methylene chain units is so effective at tuning the solubilizing power and reversed micelle morphology,
26 nanostructures of water-in-CO₂ (W/CO₂) microemulsions were investigated by high-pressure small-angle
27 neutron scattering (SANS) measurements at different water-to-surfactant molar ratios (W_0) and surfactant
28 concentrations. By modelling SANS profiles with cylindrical and ellipsoidal form factors, the FC6-
29 HC n /W/CO₂ microemulsions were found to increase in size with increasing W_0 and surfactant
30 concentration. Ellipsoidal cross-sectional radii of the FC6-HC4/W/CO₂ microemulsion droplets increased
31 linearly with W_0 , and finally reached ~ 39 Å and ~ 78 Å at $W_0 = 85$ (close to the upper limit of solubilizing
32 power). These systems appear to be the largest W/CO₂ microemulsion droplets ever reported. The aqueous
33 domains of FC6-HC6 rod-like reversed micelles increased in size by 3.5 times on increasing surfactant
34 concentration from 35 mM to 50 mM: at 35 mM, FC6-HC5 formed rod-like reversed micelles 5.3 times
35 larger than FC6-HC6. Interestingly, these results suggest that hybrid HC-chains partition into the
36 microemulsion aqueous cores with the sulfonate headgroups, or at the W/CO₂ interfaces, and so play
37 important roles for tuning the W/CO₂ interfacial curvature. The super-efficient W/CO₂-type solubilizer
38 FC6-HC4, and the rod-like reversed micelle forming surfactant FC6-HC5, represent the most successful
39 cases of low fluorine content additives. These surfactants facilitate VOC-free, effective and energy-saving
40 CO₂ solvent systems for applications such as extraction, dyeing, dry cleaning, metal-plating, enhanced oil
41 recovery and organic/inorganic or nanomaterial synthesis.



47 **Highlights**

- 48 • Anionic hybrid surfactants, FC6-HC n , were studied in supercritical CO₂ (sc-CO₂).
- 49 • FC6-HC5 having alkyl length (n) of 5 formed rod-like water-in-CO₂ (W/CO₂) microemulsion droplets.
- 50 • FC6-HC4 generated the largest globular W/CO₂ microemulsion droplets reported to date.
- 51 • FC6-HC5 was identified as the best surfactant for increasing sc-CO₂ viscosity.
- 52 • The CO₂- and hydrophobic alkyl chains play important roles for tuning W/CO₂ curvature.

53

54

55 **Keywords**

56 Supercritical CO₂, Microemulsion, Hybrid surfactant, Solubilizing power, Small-Angle Neutron

57 Scattering

58

59 1. Introduction

60 Supercritical CO₂ (scCO₂) has received much attention for its use in industrial applications owing
61 to attractive properties such as low cost, inflammability, natural abundance, high mass transfer, and
62 pressure/temperature-tunable solvency (or CO₂ density) [1]. As such, scCO₂ is currently used in numerous
63 applications including as a green solvent for organic synthesis, dry cleaning, polymerization, extraction,
64 nanomaterial processing, and enhanced oil recovery (EOR). Unfortunately, supercritical CO₂ can only
65 effectively dissolve nonpolar and small molecular mass materials [2]. The low viscosity of CO₂ is usually
66 a desirable attribute that leads to increased mass transfer. However, a significant problem when using
67 scCO₂ during enhanced oil recovery (EOR) is that the CO₂ viscosity is significantly lower than that of the
68 oil being displaced, leading to inefficient volumetric sweep of the porous media [3]. Improving the poor
69 solubility of polar materials and increasing the viscosity for EOR are both important aims for developing
70 potential applications of scCO₂. One of the most promising approaches to overcoming these limitations
71 of sc-CO₂ is to generate reversed micelles with high-polarity aqueous cores in the continuous scCO₂ phase
72 (i.e. water-in-scCO₂ microemulsions, W/CO₂ μEs) [2-3]. Such multi-component self-assembly systems
73 display not only the attractive characteristics of scCO₂, but also the solvation properties of bulk water,
74 and so they have potential as volatile organic compound (VOC)-free and energy-efficient solvents for
75 nano-material synthesis, enzymatic reactions, dry-cleaning, dyeing, and preparation of inorganic/organic
76 hybrid materials [2]. Additionally, if reversed micelles can be formed with rod-like morphologies, they
77 can also effectively enhance the scCO₂ viscosity [3]. To be a viable green and economical technology,
78 the amount of surfactant used for W/CO₂ μEs should be as small as possible. This minimal surfactant
79 concentration does however have to be balanced against the need for the large interfacial areas required
80 to form W/CO₂ μEs, and the appropriate levels of dispersed water needed to enhance process efficiencies.
81 Clearly, it is of interest to develop highly efficient surfactants for W/CO₂ μEs and formation of rod-like
82 reversed micelles, and field has been actively researched since the early 1990s [4].

83 The development of CO₂-philic hydrocarbon surfactants for scCO₂ has been recognized as an
84 important task for economic and environmental reasons [4-8]. Studies into CO₂-philic materials have been

85 performed on commercially available polymers, surfactants, and other oleo-philic substances. However,
86 those commercial compounds were basically insoluble in scCO₂ and therefore inappropriate for
87 modifying scCO₂ properties [4]. Even the common commercial surfactant Aerosol-OT (sodium bis-(2-
88 ethyl-1-hexyl) sulfosuccinate, AOT), which is widely used for water-in-oil (W/O) microemulsion
89 formulation, is inactive in scCO₂ and hence ineffective at stabilizing W/CO₂ μ Es [4]. After initial studies
90 it became apparent that conventional surfactant-design theory cannot be applied to W/CO₂ systems, and
91 that CO₂-philicity is not directly comparable to oleo-philicity. Therefore, the creation of CO₂-philic
92 surfactants has required new directions and paradigms in the field of surfactant molecular-design. Based
93 on new design principles, tailor-made surfactants able to stabilize W/CO₂ μ Es, and generate rod-like
94 reversed micelles in scCO₂ have been made [3].

95 Currently, the use of highly branched hydrocarbon chains, especially containing methyl-branches,
96 ester and ether groups, has been reported to increase surfactant solubility in scCO₂ [5-8]. Unfortunately,
97 an efficient and cost-effective hydrocarbon stabiliser for W/CO₂ μ Es, (like AOT commonly used for W/O
98 μ Es [9]) has not yet been found.

99 Many earlier studies reported that certain fluorinated surfactants, including perfluoropolyethers
100 (PFPFs) and fluorinated AOT analogues, could dissolve in CO₂ and exhibit a high W/CO₂ interfacial
101 activity, hence suggesting the feasibility of forming W/CO₂ μ Es [10-13]. The water-solubilizing power
102 in CO₂ was often discussed in terms of the water-to-surfactant molar ratio W_0 ($=[\text{water}]/[\text{surfactant}]$).
103 Hereafter, the maximal W_0 achievable in a single-phase W/CO₂ μ E, namely W_0^{max} , is used to evaluate the
104 solubilizing power. Typical benchmark values for PFPE surfactants are W_0^{max} up to ~ 20 [10-13].

105 It is not yet fully understood why fluorocarbon surfactants are so effective at stabilizing W/CO₂
106 μ Es, however, recent molecular simulation studies [14,15] have indicated that as compared with HC
107 chains, FC groups have (1), stronger interactions with CO₂ via quadrupolar and dispersion interactions,
108 and (2), weaker FC-FC chain-chain interactions due to a weak repulsion, being electrostatic in origin.
109 These properties conspire together to so that reversed micelles of FC surfactants achieve better solvation
110 by CO₂, and this, in turn, causes lower surfactant interfacial packing densities and weaker attractive inter-

micellar interactions compared with hydrocarbon surfactant analogues. However, despite these attractive properties, due to high fluorine content these F-surfactants bring disadvantages of cost and biocompatibility, thus preventing their use in applications [16]. Therefore, there is quest for CO₂-philic surfactants with as low fluorination as possible.

Other investigations [17-20] introduced a class of fluorinated AOT analogues yielding W/CO₂ μ Es with $W_0 \leq 30$ (e.g. sodium bis(1*H*,1*H*,5*H*-octafluoropentyl)-2-sulfosuccinate, di-HCF₄). Surfactants of di-HCF₄ having Co²⁺ and Ni²⁺ counter ions, Co(di-HCF₄)₂ and Ni(di-HCF₄)₂, were reported to form rod-like reversed micelles, although di-HCF₄ with Na⁺ counterions formed only globular microemulsion droplets [21,22]. This suggests exchanging monovalent counterions for divalent cations can result in viscosity-enhancing rod-like reversed micelles. In addition, double-FC-tail phosphate surfactants were also found to be efficient μ E stabilisers, the most favourable case stabilizing W_0 up to 45 [23-24].

Recently, with the aim of optimizing the surfactant structure of fluorinated AOT analogues for W/CO₂ μ Es, double-FC-tail anionic surfactants with various FC lengths, and either sulfoglutarate or sulfosuccinate headgroups, were examined [25-29]. This allowed for the effect of not only FC length, but also the addition of a methylene spacers between the double tails to be explored. This work found that the solubilizing power of the glutarates n FG(EO)₂ to be generally higher than for the succinate analogues n FS(EO)₂. The most efficient surfactant was found to be 4FG(EO)₂ which, despite having the shortest FC (perfluorobutyl) tails, could stabilize microemulsions of $W_0^{\max} = 80$ at 75°C [25]. Considering that fluorocarbons are CO₂-philic groups and longer FC surfactants generally have higher solubilizing power [25-29], the fact that this high stability can be obtained with only the shortest chain FC 4FG(EO)₂ is at first sight surprising. In further studies, the minimum fluorine content necessary to render a surfactant CO₂-philic has been identified by using double-pentyl-tail surfactants with different fluorination levels [30,31]. In these surfactants, at least two fluorinated carbons (CF₃CF₂-) were required to stabilise W/CO₂ μ Es. Through these studies, the understanding behind the effect of FC-tail length on W/CO₂ μ Es stabilization and solubilizing power and for symmetrical double FC-tail surfactants (i.e. fluorinated AOT-analogues) is improving.

137 As for the fully fluorinated surfactant series, two-tail hybrid surfactants, having separate HC and
138 FC chains in the same molecule, have also been evaluated for stabilization of W/CO₂ μ Es. The first
139 successful example of a CO₂-philic hybrid surfactant was sodium 1-pentadecafluoroheptyl-1-
140 octanesulfate (F7H7, (C₇H₁₅)(C₇F₁₅)CHOSO₃Na), which solubilized water up to $W_0^{\max} = 35$ [32]. Further
141 studies [3,33,34] of hybrid surfactants related to F7H7 but with different FC and HC chain lengths, M-
142 FmH4 (Counter ion M= Li, Na, and K, fluorocarbon length $m = 7$ and 8), observed the formation of
143 W/CO₂ μ Es for most of the analogues, but with smaller attainable W_0^{\max} values than for F7H7. On the
144 other hand, these hybrid surfactant systems were often reported to form elongated reversed micelles
145 [3,33,34], whereas those formed by regular non-hybrid surfactants were likely to be spherical. The
146 formation of elongated aggregates with a high aspect ratio (rod length/diameter) can serve to thicken
147 dense CO₂, and appears to be a viable way to achieve higher efficiencies in EOR applications [3].
148 Unfortunately, these unique characteristics have never been examined in detail in terms of the hybrid tail
149 structure (e.g. effect of FC and HC length and the balance of both).

150 Recently, a series of hybrid surfactants, sodium 1-oxo-1-[4-(perfluoroalkyl)phenyl]alkane-2-
151 sulfonates, FC m -HC n (FC length $m = 4, 6$, HC length $n = 2, 4, 5, 6$ and 8) were used to clarify the effects
152 of FC and HC chain length on the phase stability and nanostructures of the reversed micelles formed
153 [26,35]. The optimal HC-tail and FC-tail length in this hybrid surfactant was found to be $n = 4$ and $m = 6$
154 respectively (i.e. FC6-HC4). This surfactant was able to yield μ Es with a maximum solubilizing power,
155 W_0^{\max} of 80; a value equal to the highest performance yet reported in W/CO₂ systems [3-35]. The
156 identification of an optimal HC-length is very interesting, since straight-chain HCs were commonly
157 considered not to be CO₂-philic [4] and their inclusion in FC-surfactant molecules was intentionally
158 limited in order to retain CO₂-philicity. To evaluate the effectiveness per F-atom the solubilizing power
159 per F-atom was estimated as 6.2/F atom, which is ~ 1.5 times larger than the most effective FC-surfactant
160 found in earlier papers [10-35]. The highest effectiveness per F-atom generated by hybrid structures is
161 also an interesting concept design of new CO₂-philic surfactants. High pressure-small angle neutron
162 scattering (HP-SANS) measurements [35] was used to size the D₂O cores of FC6-HC n reversed micelles

163 at $W_0 = 20$, and gave evidence for shape transitions in core morphology after increasing HC-tail length
164 (ellipsoid for $n = 4 \rightarrow$ cylinder for $n = 5$ and $6 \rightarrow$ sphere for $n = 8$). The micelle shape-anisotropy and
165 aspect ratio were seen to reach a maximum of 6.3 at a HC-tail length $n = 6$.

166 How does a hybrid surfactant stabilise W/CO₂ μ Es and also form elongated reversed micelles?
167 What is the role of the non-CO₂-philic HC-tails? Although these questions have not yet been clarified,
168 they remain interesting and important topics for chemists in this field. To improve understanding about
169 CO₂-philic surfactant design, this study has focused on the effect of the hybrid tail structure (e.g. FC-HC
170 balance) on solubilizing power, micellar aggregate size and shape in scCO₂. This provides important
171 information on structure-property relationships for hybrid surfactants such as hydrophilic/CO₂-philic
172 balance (HCB) [36], critical packing parameter (CPP) [37], interactions between tail-tail and tail-head
173 groups [38]. This is an important step in obtaining optimized, super-efficient, low fluorine content
174 surfactants for applications of W/CO₂ μ Es and CO₂-based fluids in general.

175 With the aim of clarifying the role of the HC-tail in hybrid surfactants, this study has examined
176 reversed micelle nanostructures and molecular properties (i.e. CPP and area per molecule) of FC₆-HC_{*n*} in
177 water/supercritical CO₂ mixtures using HP-SANS measurements and detailed SANS data analyses. The
178 findings described here suggest new directions and strategies for developing CO₂-philic surfactants for
179 stabilizing μ Es and elongated reversed micelles, both of which are applicable to many practical
180 applications.

181

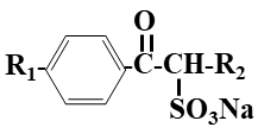
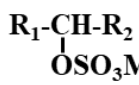
2. Experimental Section

2.1. Materials

The family of surfactants studied here are hybrid surfactant sodium 1-oxo-1-[4-(perfluoroalkyl)phenyl]alkane-2-sulfonates, FC m -HC n (FC length $m = 6$, HC length $n = 4, 5, 6$ and 8). The surfactants FC m -HC n with $m/n = 6/6$, and $6/8$ were provided by Prof. Yoshino and Dr. Kondo at Tokyo University of Science [39]. The other surfactants FC6-HC4 and FC6-HC5 were synthesised and purified as described in the reference [35].

Structures of FC m -HC n and the other control hybrid surfactants F m H n are shown in **Table 1** along with the interfacial properties of aqueous solutions obtained by standard measurements [3,33-35,40,41]. Ultrapure water with a resistivity of 18.2 M Ω cm was obtained from a Millipore Milli-Q Plus system. CO₂ was of > 99.995% purity (Taiyo Nippon Sanso Corp.). The structures of the steric models and the length of surfactant molecules (in isolation) were calculated by MM2 (Molecular Mechanics program 2) calculations (Chem 3D; CambridgeSoft Corp., Cambridge, MA).

Table 1 Interfacial properties of hybrid surfactants FC n -HC m and F m H n in water at 25 °C.

Main structure	Surfactant	R ₁ / R ₂	T _K ^{a)} / °C	CMC ^{b)} / M	γ_{CMC} ^{c)} /(mN m ⁻¹)	A _{A/W} ^{d)} / Å ²
	FC6-HC4	F(CF ₂) ₆ - / H(CH ₂) ₄ -	15	2.3 × 10 ⁻⁴	20.4	105
	FC6-HC5	F(CF ₂) ₆ - / H(CH ₂) ₅ -	10	1.3 × 10 ^{-4 e)}	18.0 ^{e)}	72 ^{e)}
	FC6-HC6	F(CF ₂) ₆ - / H(CH ₂) ₆ -	48	5.5 × 10 ^{-5 f)}	16.2 ^{f)}	98 ^{f)}
	FC6-HC8	F(CF ₂) ₆ - / H(CH ₂) ₈ -	> 95	—	—	—
	Li-F7H4 (M=Li)	F(CF ₂) ₇ - / H(CH ₂) ₄ -		2.2 × 10 ⁻³	26.0	106
	K-F7H4 (M=K)	F(CF ₂) ₇ - / H(CH ₂) ₄ -		1.4 × 10 ⁻³	22.1	62
	Na-F7H4 (M=Na)	F(CF ₂) ₇ - / H(CH ₂) ₄ -		1.9 × 10 ⁻³	23.8	67
	Na-F8H4 (M=Na)	F(CF ₂) ₈ - / H(CH ₂) ₄ -		7.8 × 10 ⁻⁴	25.4	68

^{a)} Krafft temperature, ^{b)} Critical micelle concentration in water. ^{c)} Surface tension at CMC. ^{d)} Molecular area at CMC obtained by using the Gibbs adsorption equation. The uncertainties of A_{A/W} are ±5 Å². ^{e)} at 35 °C. ^{f)} at 50 °C.

2.2 High-Pressure Small-Angle Neutron Scattering (HP-SANS) measurements and data analysis

Due to the range of neutron wavelengths available, time-of-flight SANS is suitable for studying the shapes and sizes of colloidal systems. High-pressure SANS (HP-SANS) is a particularly important technique for determining aggregate nanostructure in supercritical CO₂. The HP-SANS measurements of the D₂O/hybrid compound/scCO₂ systems were performed at 45 °C at various pressures. The LOQ and the SANS2D time-of-flight instruments, at the Rutherford Appleton Laboratory at ISIS UK, were used in conjunction with a stirred, high-pressure cell (Thar). The path length in the cell and neutron beam diameter were both 10 mm. The measurements gave absolute scattering cross sections $I(Q)$ (cm⁻¹) as a function of momentum transfer Q (Å⁻¹), which is defined as $Q = (4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle. The accessible Q ranges were 0.007-0.22 Å⁻¹ for LOQ and 0.002-1.0 Å⁻¹ for SANS2D arising from an incident neutron wavelength, λ , of 2.2-10 Å. The data were normalised for transmission, empty cell, solvent background, and pressure induced changes in cell volume as before [19-23,29-31,33-35].

Pre-determined amounts of D₂O and surfactant, where the molar ratios of surfactant to CO₂ were fixed at 8.0×10^{-4} , 1.7×10^{-3} and 2.4×10^{-3} (= 17, 35 and 50 mM at the appropriate experimental condition, respectively), were loaded into the Thar cell. Then, CO₂ (11.3g), was introduced into the cell by using a high pressure pump, and the surfactant/D₂O/CO₂ mixture was pressurised to 350 bar at 45 °C by decreasing the inner volume of the Thar cell. With vigorous stirring, visual observation was carried out to identify if any mixture was either a transparent single-phase (W/CO₂ μE), or a turbid phase-separate system. Finally, the HP-SANS experiments were performed for not only single-phase W/CO₂μEs, but also the turbid phases formed below the cloud point phase transition pressure P_{trans} . Due to the systems being dilute dispersions (volume fractions typically 0.05 or less), the physical properties of the continuous phase of scCO₂ were assumed to be equivalent to those of pure CO₂.

Scattering length densities of surfactants, CO₂ and D₂O were calculated as in supplementary data (See section S1). The shells of FC6-HC_{*n*}/D₂O/CO₂ μEs were estimated to be composed of the perfluorohexyl-phenylene groups, and the scattering length density, ρ_{shell} , was calculated as 2.69×10^{10}

227 cm^{-2} from equation (S1) in supplementary data. The average mass densities values of benzene and
228 perfluorohexane at 25 °C were 0.88 g and 1.67 g cm^{-3} respectively [42]. As ρ_{shell} was close to ρ_{CO_2} (2.29
229 $\times 10^{10} \text{ cm}^{-2}$) and the shells are solvated with CO_2 to get both scattering length densities closer, neutron
230 scattering from the shells was identified to be negligible. Therefore SANS from the $\text{D}_2\text{O}/\text{CO}_2$ μEs was
231 assumed to only be from the so-called aqueous core contrast.

232 For model fitting data analysis, the W/CO_2 μE droplets were treated as cylindrical or ellipsoidal
233 particles with a Schultz distribution in core radius and length [43]. The polydispersities in ellipsoid and
234 cylinder radii and cylinder length were fixed at 0.3 as found in spherical $\text{D}_2\text{O}/\text{CO}_2$ μEs with the double
235 FC-tail surfactants (polydispersity = 0.17-0.40) [29, 35, 44]. Full accounts of the scattering laws are given
236 elsewhere [43, 44].

237 Data have been fitted to the models described above using the SasView small-angle scattering
238 analysis software package (<http://www.sasview.org/>). The fitted parameters are the core radii
239 perpendicular to the rotation axis ($R_{\text{f-ell,a}}$) and along the rotation axis ($R_{\text{f-ell,b}}$) for ellipsoidal particles, or
240 the core radius R_{cyl} and the length L_{cyl} for cylindrical particles; these values were initially obtained by
241 preliminary Guinier analyses ($L_{\text{g-disk}}$, $R_{\text{g-disk}}$, and $R_{\text{g-sph}}$) [29,35,44,45].

242

3. Results and Discussion

3.1 Growth and morphology changes for FC6-HC n /W/CO $_2$ μ Es with loading water

To examine changes in the shape and size of D $_2$ O/CO $_2$ μ Es with FC6-HC4 and FC6-HC6 as a function of W_0 , SANS $I(Q)$ profiles with different W_0 values were measured at a constant surfactant concentration of 16.7 mM at 45 °C and 350 bar. SANS data along with the fitted $I(Q)$ functions are shown in **Figure 1**.

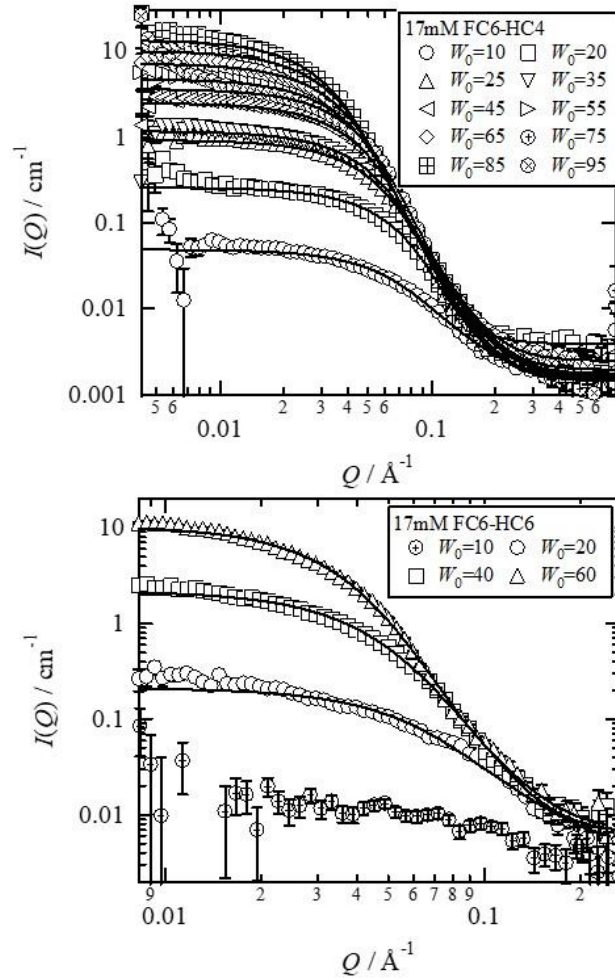


Figure 1. SANS profiles for FC6-HC n ($n = 4$ or 6)/D $_2$ O/CO $_2$ mixtures with different W_0 values at 45 °C and 350 bar (CO $_2$ density = 0.92 g/cm 3). Fitted curves were based on a model incorporating a Schultz distribution of polydisperse ellipsoid particles. The molar ratio of the surfactant to CO $_2$ was fixed at 8×10^{-4} ([Surfactant] = \sim 16.7 mM at the experimental conditions).

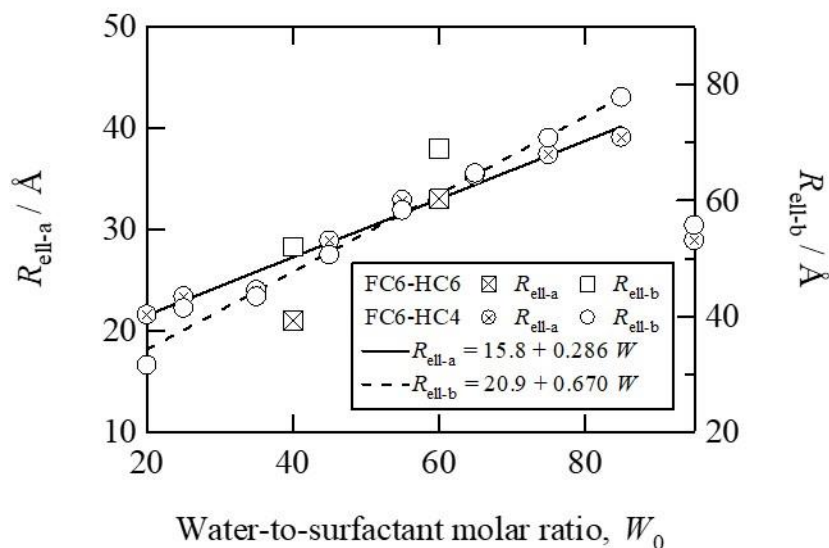
255 SANS profiles are useful in determining the shape of nano- and colloidal particles. With W_0 values
 256 lower than their maximum solubilizing powers ($W_0^{\max} = 80$ for FC6-HC4 and 55 for FC6-HC6 under the
 257 experimental conditions [35]), FC6-HC4 and FC6-HC6 exhibited transparent single-phases giving
 258 distinct SANS profiles. Although turbid phases appeared as W_0 exceeds W_0^{\max} , a SANS curve from D₂O
 259 droplets was still observed. In the low Q region for FC6-HC4, the scattering intensity increased with W_0
 260 until $W_0 = 85$, suggesting growth of the μ E droplets with increased water loading. The analysis of SANS
 261 profiles clearly demonstrated the highest solubilizing power $W_0^{\max} = 80$ of FC6-HC4 in surfactant/scCO₂
 262 systems ever reported.

263 In the low Q region (typically in the case of droplet μ Es $< 0.01 \text{ \AA}^{-1}$), the scattering may scale as
 264 $I(Q) \sim Q^{-D}$, where D is a characteristic “fractal dimension” for the colloids; hence, the gradient of a log-
 265 log plot will be $-D$. In the case of non-interacting spheres, D should be zero in this low Q region, whereas
 266 $D = 1$ for cylinders and 2 for disks [29, 35, 44, 45]. The SANS profiles for FC6-HC4 and FC6-HC6 at
 267 16.7mM show $D = 0$ and 1, suggesting the presence of globular or rod-like nanodomains, respectively.
 268 Methods exist to approximate radius from SANS data for globular μ Es using Guinier plots [29, 35, 44,
 269 45] ($\ln [I(Q)]$ vs Q^2) and Porod plots ($I(Q) Q^4$ vs Q) as shown in supplementary data (**Figures S1** and
 270 **S2**). Radii of gyration (R_g) and sphere radius ($R_{g\text{-sph}}$) from Guinier plots and sphere radius (R_{prd}) from
 271 Porod plots are presented in **Table S1** in supplementary data. The radii R_g and R_{prd} were similar at same
 272 W_0 , lending confidence to these analyses.

273 The values of R_{prd} or R_g were employed as the starting points for model fit analyses using the full
 274 polydisperse Schultz ellipsoid or cylinder models. The parameter outputs are the average values of radii
 275 for the ellipsoidal D₂O cores ($R_{\text{ell,a}}$ and $R_{\text{ell,b}}$) or, where used, the radius and length of the cylindrical core
 276 (R_{cyl} and L_{cyl}). The polydispersity width was set at 0.3, which is a typical value for W/CO₂ μ E systems
 277 (e.g. 0.17-0.40 for double FC-tail sulfonate surfactants [29,35,44]). These fitted parameters are also listed
 278 in **Table S1**.

279 When increasing W_0 from 25 to 95, for FC6-HC4, the ellipsoid radii gradually increased but the
 280 aspect ratios ($R_{\text{ell-b}} / R_{\text{ell-a}}$) of the D₂O core was lower than two and comparable between samples. This

281 suggests a more globular, rather than elongated shape. However, this globular shape μ E transformed into
 282 rod-like on decreasing the W_0 value to 10, or by increasing the HC-tail length from 4 to 6 to with surfactant
 283 FC6-HC6. This is reflected in the SANS data which for FC6-HC4 at $W_0 = 10$, and FC6-HC6 at $W_0 = 20$
 284 were both well fitted using the cylindrical form factor model rather than the ellipsoidal one.



286
 287 **Figure 2.** Changes in ellipsoidal aqueous core radii $R_{\text{ell-a}}$ and $R_{\text{ell-b}}$ for the 16.7 mM FC6-HC n /D₂O/CO₂
 288 μ Es as a function of W_0 at 45 °C and 350 bar. The data were taken from **Table S1**. Solid and broken lines
 289 show linear functions fitted with the data for FC6-HC4 and FC6-HC6, respectively.

290
 291 To clarify the growth of μ E droplets with loading water, changes in radii $R_{\text{ell-a}}$ and $R_{\text{ell-b}}$ of the
 292 ellipsoid D₂O cores were plotted as a function of W_0 in **Figure 2**. In the case of the FC6-HC4/W/CO₂ μ E,
 293 both radii increased with W_0 linearly; $R_{\text{ell-a}} = 15.8 + 0.286 W_0$ and $R_{\text{ell-b}} = 20.9 + 0.670 W_0$. Eventually,
 294 $R_{\text{ell-a}}$ and $R_{\text{ell-b}}$ reached 39.1 Å and 77.8 Å at $W_0 = 85$ (\approx the maximum solubilizing power), identified as
 295 the largest core radius ever reported in a W/CO₂ μ E systems [10-35]. Previous SANS studies dealing with
 296 double FC-tail surfactants n FG(EO)₂ with differing FC lengths ($n = 4-8$) found a linear relationship
 297 between spherical D₂O core radius, R_c , and W_0 where $R_c = a + b W_0$, where the constants $a = 5.0-5.4$ and
 298 $b = 0.60-0.64$ [29]. When comparing the average values of the constants, $\langle a \rangle$ and $\langle b \rangle$ found for

299 $n\text{FG}(\text{EO})_2$ to the values found here for FC6-HC4 ($\langle a \rangle = 18.4$, $\langle b \rangle = 0.478$), $\langle b \rangle$ for FC6-HC4 was
300 slightly smaller than b for $n\text{FG}(\text{EO})_2$ but the $\langle a \rangle$ value was approximately 3.6 times larger than the a
301 value. The constants a and b are known to strongly depend on volume of surfactant headgroup (v_{head}) and
302 area per surfactant molecule (A), respectively, as shown in the relationship

$$303 \quad \alpha(p) R_c = (3v_{\text{head}}/A) + (3v_w/A) W_0 \quad (1)$$

304 where $\alpha(p) = 1 + 2p^2$, p is polydispersity index (σ/R_c), R_c is core radius, and v_w is volume of a water
305 molecule [29,47]. Namely, the larger $\langle a \rangle$ and the smaller $\langle b \rangle$ values suggests FC6-HC4 to have a larger
306 v_{head} and a smaller A than each value of $n\text{FG}(\text{EO})_2$. Based on equation (3), volume-to-surface area ratio
307 per aqueous core in reversed-type μE ($v_{\text{core}}/s_{\text{core}}$) can be expressed as,

$$308 \quad \alpha(p) (v_{\text{core}}/s_{\text{core}}) = (v_{\text{head}} N_{\text{agg}} + v_w W_0 N_{\text{agg}}) / (A N_{\text{agg}}) = (v_{\text{head}}/A) + (v_w/A) W_0 \quad (2)$$

309 where N_{agg} is aggregation number. One advantage of using equation (2) is that it can be applied to a wide
310 range of morphologies (spheres, ellipsoids, rods etc) whereas equation (1) is just for spherical reversed-
311 type μEs . For detailed examination of v_{head} and A for FC6-HC n , ($v_{\text{core}}/s_{\text{core}}$) values calculated from $R_{\text{ell-a}}$
312 and $R_{\text{ell-b}}$ were plotted as a function of W_0 , and displayed in **Figure 3**.

313

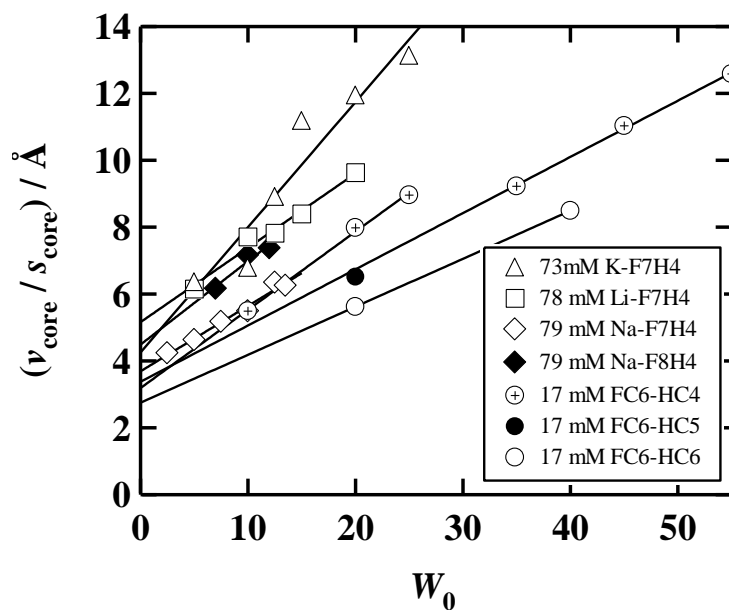


Figure 3. Relationship between volume-to-surface area ratio ($v_{\text{core}}/s_{\text{core}}$) of aqueous cores and W_0 for the 17mM FC6-HC $_n$ /D₂O/CO₂ μ Es at 45 °C and 350 bar. The $v_{\text{core}}/s_{\text{core}}$ values were calculated with ellipsoidal core radii listed in **Table S1**. The graph also displays data for D₂O/CO₂ μ Es with 73 mM K-F7H4, 78 mM Li-F7H4, 75-79 mM Na-F7H4, 79 mM Na-F8H4 at 23-40 °C and 380-400 bar reported in earlier papers [3,33,34].

Figure 3 also includes data for hybrid surfactants FC6-HC5, and M-F n H4 (CF₃(CF₂) $_m$ -CH(-OSO₃M)-(CH₂)₃CH₃, $m = 7$ or 8 , $M = \text{K, Li, or Na}$) reported in earlier papers [3,33,34]. Most ($v_{\text{core}}/s_{\text{core}}$) data in **Fig 3** could be expressed as linear functions, suggesting v_{head} and A can be calculated using equation (2). **Table 2** lists the values for area per surfactant molecule ($A_{\text{v/s}}$), v_{head} , and radius of headgroup ($R_{\text{head}} = (3v_{\text{head}} / 4\pi)^{1/3}$) as obtained from the slopes and intercepts in **Fig. 3**.

Table 2 Area per surfactant molecule ($A_{v/s}$), volume (v_{head}) and radius (r_{head}) of surfactant headgroup at W/CO₂ interface.

Surfactant	Conc. / mM	W_0	$A_{v/s}$ / Å ²	v_{head} / Å ³	r_{head} / Å
FC6-HC4* ¹	17	10-25	109	410	4.6
		35-55	152	600	5.2
FC6-HC6* ¹	17	20-40	177	580	5.2
K-F7H4* ²	73	5-25	68	340	4.3
Li-F7H4* ²	78	5-20	115	700	5.5
Na-F7H4* ²	79	7-12	130	570	5.1
Na-F8H4* ²	79	2.5-13.5	102	540	5.1

329

330 $A_{v/s}$ is area per surfactant headgroup obtained from the slopes, and v_{head} and r_{head} are volume and radius
331 (if sphere model used) of headgroup from the intercepts in **Fig. 3**. The uncertainties of $A_{v/s}$, v_{head} , and r_{head}
332 are ± 10 Å, ± 30 Å³, and ± 0.3 Å. *¹ at 45 °C and 350 bar, *² at 30 °C and 500 bar

333

334

335 In the case of FC6-HC4, there are two linear functions describing the data; one for samples with W_0 values
336 between 10 and 25 and one for W_0 values between 35 and 55. Both $A_{v/s}$ and v_{head} for data in the high W_0
337 region are larger by 1.4-1.5 when compared to data in the low W_0 region. This increase in area per
338 surfactant molecule with W_0 was also found in A_{prd} values obtained from Porod analysis [46] (**Table S1**,
339 **Figure S2**) and in earlier W/CO₂ μE studies [29, 44]. The trend most likely points to the swelling
340 behaviour of the headgroup with water and counter-ion dissociation. When comparing between FC6-HC4
341 and FC6-HC6, $A_{v/s}$ for FC6-HC6 was larger at $W_0=35-55$ in spite of the similar v_{head} and r_{head} values. The
342 structural difference between both surfactants is just an ethylene unit in the HC-tail. Therefore, the
343 increased $A_{v/s}$ results not from the headgroup but the increased bulkiness of the hydrophobic tail. As
344 suggested in earlier studies [35, 47], this implies that when absorbed at the water interface, the HC-tails
345 of the FC6-HC n are oriented toward the lateral direction (see **Figure S3** in supplementary data).

346 M-FmH4 are a series of hybrid surfactants having a slightly longer FC-chain, with a sulphate
347 headgroup and no aromatic ring. When comparing FC6-HC4 and Na-F7H4 (which have similar
348 structures) $A_{v/s}$ and v_{head} (or r_{head}) for FC6-HC4 at $W_0 \leq 25$ are lower than those of Na-F7H4, resulting
349 from the smaller sulfonate headgroup of FC6-HC4. Counterion effects can also be found in the values of
350 v_{head} (or r_{head}) in M-F7H4 surfactants with K^+ , Na^+ , and Li^+ . The v_{head} (or r_{head}) value increases in the order
351 of $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. The order is likely to relate to the Hofmeister series [48], or degree of counterion
352 dissociation of the sulfate group, that is $\text{Li}^+ > \text{Na}^+ > \text{K}^+$.

353

3.2 Elongation of FC6-HC n reversed micelles with increasing surfactant concentration

Earlier studies of W/CO₂ μ Es found that with fluorinated surfactants, rod-like reversed micelles often form at low W_0 values of ~ 10 [3,21,22,33-35]. Previous SANS studies [35] revealed FC6-HC5 and FC6-HC6 to also form reversed micelles with aqueous core aspect ratios larger than 5, even at a low surfactant concentration of 16.7 mM and a relative high W_0 value of 20. To examine the formation of longer rod-like micelles at high surfactant concentrations, SANS measurements were performed with 35 mM or 50 mM FC6-HC n /D₂O/CO₂ mixtures at $W_0 = 10$, 45 °C and 350 bar. These SANS profiles are presented in **Figure 4**.

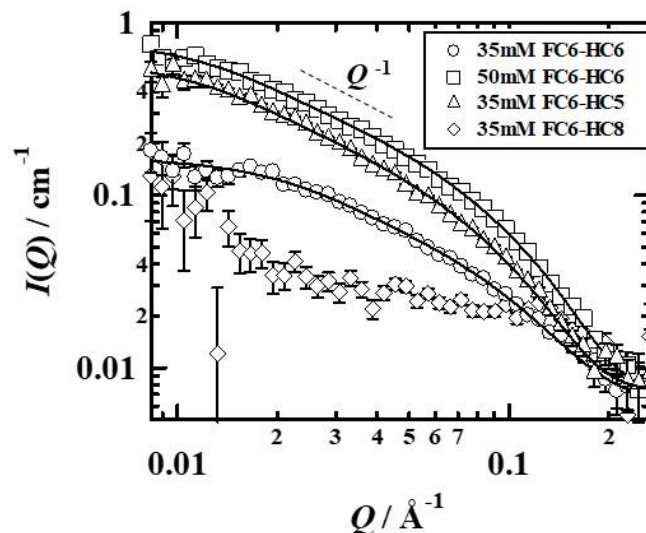


Figure 4. SANS profiles for 35 mM and 50 mM FC6-HC n ($n = 5, 6$ or 8)/D₂O/CO₂ mixtures with $W_0 = 10$ at 45 °C and 350 bar (CO₂ density = 0.92 g/cm³). Fitted curves were based on a model incorporating a Schultz distribution of cylindrical particles (polydisperse).

The poor solubility of FC6-HC8 in scCO₂ gave a turbid two-phase system and noisy SANS profiles. However, the shorter HC-tails of $n \leq 6$ allowed for the formation of one-phase W/CO₂ μ Es in spite of high surfactant concentrations of 35 mM and 50mM. These systems display distinct SANS profiles with scaling as $\sim Q^{-1}$ over the intermediate Q -range, suggesting the formation of rod-like reversed micelles

[29,35,44,45]. To estimate radius/length for rod-like reversed micelles, Guinier plots of $\ln [I(Q) Q]$ vs Q^2 and $\ln [I(Q) Q]$ vs Q^2 were prepared (**Figure S4**). The SANS profiles were also analysed by fitting with theoretical curves of a cylinder particle model. Rod length and radius obtained by Guinier analysis were once again employed as a starting point for the curve fitting.

Table 3 Radii, lengths, aspect ratios (X_{micelle} and X_{core}), intrinsic viscosity $[\eta]$ and specific viscosity η_{sp} for rod-like reversed micelles and cores in FC6-HC n /D₂O/CO₂ mixtures with $W_0=10$ at 45 °C and 350 bar.

n	[FC6-HC n] / mM	Guinier			Curve fitting		Aspect ratio		Viscosity	
		R_g / Å	L_{gui} / Å	R_{gui} / Å	L_{cyl} / Å	R_{cyl} / Å	X_{core}	X_{shell}	$[\eta]$	η_{sp}
5	35	70.1	243	20.8	879	12.2	36.0	17.7	30.9	2.07
6	35	30.4	105	31.4	166	12.0	7.0	3.8	4.4	0.24
	50	66.5	230	22.1	583	10.8	26.9	12.6	18.9	1.28
8	35	34.4	119	30.6	—	—	—	—	—	—

R_g , L_{gui} and R_{gui} are radius of gyration, rod length and rod radius respectively as obtained from the slopes of Guinier plots. L_{cyl} and R_{cyl} are cylinder length and radius when the experimental data were fitted by theoretical curve to a cylindrical particle model. Aspect ratios of core (X_{core}) and shell (X_{shell}) are calculated as $L_{\text{cyl}}/(2R_{\text{cyl}})$ and $(L_{\text{cyl}}+2l_{\text{tail}})/\{2(R_{\text{cyl}}+l_{\text{tail}})\}$, respectively. The surfactant tail length l_{tail} is identified as 13.4 Å from the perfluorohexyl phenyl tail length [35]. Intrinsic viscosity $[\eta]$ and specific viscosity η_{sp} were calculated from equations (4) and (7), respectively.

Table 3 shows lengths, radii and aspect ratios of D₂O cores in rod-like reversed micelles given by Guinier and curve fitting analyses. Focusing on the core radius obtained from curve fitting, the radii at $W_0 = 10$ were almost constant at 10.8-12.2 Å, independent of concentration and HC-tail length of FC6-HC n . On the other hand, the length of FC6-HC6 reversed micelles increased by 3.5 times (166 Å \rightarrow 583 Å)

when increasing surfactant concentration from 35 mM to 50 mM. When comparing FC6-HC5 and FC6-HC6 reversed micelles at 35 mM, FC6-HC5 formed rod-like reversed micelles 5.3 times longer than that of FC6-HC6. The longest rod-like reversed micelles in a W/CO₂ system previously reported was formed with the double-fluorinated tail surfactant with Ni²⁺ counterion, Ni(di-CF₄)₂, with the length reaching 600 Å at a surfactant concentration of 50 mM with W₀ = 5 at 25 °C and 400 bar [21,22]. Interestingly, the core length of FC6-HC5 reversed micelles has surpassed this value with the length reaching an unprecedented value of ~880 Å which is the new longest rod length ever reported in a W/CO₂ microemulsion.

In general, the viscosities of colloidal dispersions depend on particle concentration, shape and effective volume. Even in the case of rod-like reversed micelle/scCO₂ systems, a clear relationship between viscosity and aspect ratios of reversed micelles is apparent, and this is described in the supplementary data (**Figure S5**). To normalize for concentration, it is helpful to evaluate an intrinsic viscosity $[\eta]$ at infinite dilution. To estimate the CO₂-thickening ability of the FC6-HC5 reversed micelles, $[\eta]$ and viscosity of reversed micelle/CO₂ solutions were approximated as described below [21,49]. The $[\eta]$ value is very sensitive to particle shape, for hard spheres $[\eta] = 2.5$, whereas for one-dimensional, anisotropic particles $[\eta]$ is greater than this and can be approximated using equation (3) [50,51]:

$$[\eta] = 2.5 + 0.4075 (X_{\text{micelle}} - 1)^{1.508} \quad (3)$$

where X_{micelle} is the aspect ratio of the reversed micelle in **Table 3**. The $[\eta]$ value can be used to estimate η_{sp} based on the structural parameters derived from SANS analysis and the known volume fraction ϕ_p . As such, equation (4) details an approximate formula which is valid for the dilute regime of $\phi_p < 0.2$, and the calculated viscosity has been confirmed to be coincident with the experimental data [52].

$$\eta_{\text{sp}} = [\eta] \phi_p + K_H [\eta]^2 \phi_p^2 \quad (4)$$

where the K_H is the Huggins coefficient for rods (in this case ~0.4) [51], calculated from and estimated shear rate and rotational diffusion coefficient D_{rot} ; shear rate being obtained by analytical solution of the Navier–Stokes equation and D_{rot} being calculated using the SANS structural parameters and neat solution viscosity. The values ϕ_p can be calculated by following equation.

$$\phi_p = C_{\text{micelle}} V_{\text{micelle}} \quad (5)$$

420 where V_{micelle} and C_{micelle} are molar volume and molar concentration of micelle, respectively. Those are
 421 obtained by equations (6) and (7) [29,35,53].

$$422 \quad V_{\text{micelle}} = v_{\text{micelle}} N_A = \pi (R_{\text{cyl}} + l_{\text{tail}})^2 (L_{\text{cyl}} + l_{\text{tail}}) N_A \quad (6)$$

$$423 \quad C_{\text{micelle}} = (V_{\text{D2O}} C_{\text{D2O}} + V_{\text{head}} C_{\text{surf}}) / (V_{\text{core}}) = C_{\text{surf}} (V_{\text{D2O}} W_0 + v_{\text{head}} N_A) / (v_{\text{core}} N_A) \quad (7)$$

424 where v_{micelle} is particle volume of micelle, l_{tail} is surfactant tail length (identified as 13.4 Å for FC6-HC n
 425 series from the perfluorohexyl phenyl part [35]), N_A is Avogadro's number, C_{surf} and C_{D2O} , C_{micelle} are
 426 molar concentrations of surfactant, D₂O and reversed micelle, V_{D2O} , V_{head} , and V_{core} are molar volumes of
 427 D₂O, surfactant headgroup and D₂O core, v_{core} and v_{head} are volumes per D₂O core ($V_{\text{core}} = v_{\text{core}} N_A$) and
 428 headgroup ($V_{\text{head}} = v_{\text{head}} N_A$), respectively. The v_{core} values were calculated using radii and lengths obtained
 429 by the curve fitting, and the v_{head} values were referred from **Table 2**.

430 **Table 3** also shows the viscosities, $[\eta]$ and η_{sp} , of the FC6-HC n rod-like reversed micelle/CO₂
 431 solutions calculated from the equations (3) and (4), respectively. The viscosities at 35 mM were $[\eta] = 30.9$
 432 and $\eta_{\text{sp}} = 2.07$ for the FC6-HC5 rod-like reversed micelles with the longest length $L_{\text{cyl}} = 879$ Å. These
 433 values are larger by 7.0 and 8.6 times respectively than for the FC6-HC6 micelles. An earlier paper [34]
 434 reported the largest viscosity enhancement of $\eta_{\text{sp}} = 1.0$ for the 75 mM Na-F7H4/W/CO₂ systems with W_0
 435 = 12.5. However, the η_{sp} value of the FC6-HC5/W/CO₂ system now achieves and even greater viscosity
 436 enhancement.

437

3.3 Change in CPP, aggregation number, elongation of FC6-HC n reversed micelles with increasing surfactant concentration

The results in Sec 3.1-3.2 suggest the optimal HC-tail lengths to solubilize water and to form rod-like reversed micelles in scCO₂ is where $n = 4$ and 5, respectively. Why do these specific HC-tail lengths drive the water solubilization and the elongation of reversed micelles? A key to resolving this question may be in characteristics special to hybrid surfactants. For example, HC-tails in self-assembled hybrid surfactants may line up in the direction towards the reversed micelle centre (i.e. aqueous core) or the shell (i.e. CO₂-phase).

To investigate the HC-tail arrangement using aggregation properties of FC6-HC n ($n = 4, 5, 6$) in scCO₂, the aggregation number of surfactant per reversed micelle (N_{agg}) and occupied area per surfactant molecule at the W/CO₂ μ E surface ($A_{C/W}$) were calculated by following equations.

$$N_{agg} = C_{surf}/C_{micelle} \quad (8)$$

$$A_{C/W} = s_{core}/N_{agg} \quad (9)$$

According to critical packing parameter (CPP) theory [37], CPP can be also obtained by

$$CPP = v_{tail}/(A_{C/W} l_{tail}) \quad (10)$$

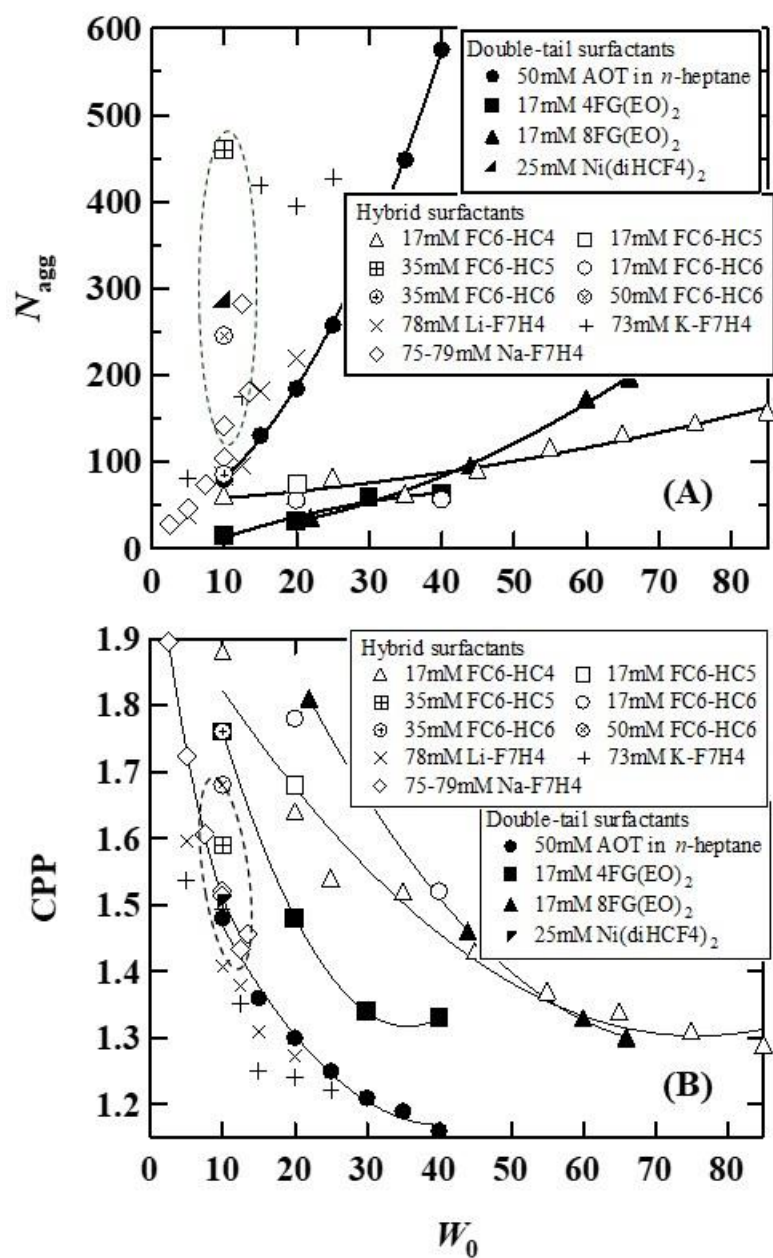
where v_{tail} and l_{tail} are hydrophobic tail volume and length, respectively. According to this approach reversed micelles would be formed for surfactants with $CPP > 1$ (reversed cones form if the double-tail orients upward) to ~ 1 (cylindrical). If the hydrophobic part is assumed to be a truncated core, the volume should be [29,35,53]

$$v_{tail} = l_{tail} \{ A_{C/W} + A_{tail} + (A_{C/W} A_{tail})^{0.5} \} / 3 \quad (11)$$

where A_{tail} is area per hydrophobic tail terminus, respectively. Then eq.(10) can be simply expressed as

$$CPP = \{ s_{micelle} + s_{core} + (s_{micelle} s_{core})^{0.5} \} / (3s_{core}) \quad (12)$$

where $s_{micelle}$ is the surface area per reversed micelle [29,35,53]. In this study, the values of $s_{micelle}$ were calculated from the shape parameters ($R_{f-ell,a}$, $R_{f-ell,b}$, R_{f-cyl} , and L_{f-cyl}) and surfactant tail length l_{tail} assumed to be 13.4 Å (the length between the terminal F-atom and the C-atom bearing the sulfonate group [35]). The calculated aggregation properties N_{agg} , $A_{C/W}$, and CPP are listed in **Table S2** (supplementary data).



466

467 **Figure 5.** Changes in (A) aggregation number N_{agg} of reversed micelles and (B) critical packing parameter
 468 CPP as a function of W_0 for D₂O/CO₂ μ Es with hybrid and double-tail surfactants or D₂O/*n*-heptane μ Es
 469 with AOT. Experimental conditions were 45 °C and 350 bar for 17mM FC6-HC_n ($n = 4-6$) and 17mM
 470 n FG(EO)₂ ($n = 4, 8$), 23-40 °C and 380-400 bar for 78 mM Li-F7H4 and 73 mM K-F7H4, 75-79 mM Na-
 471 F7H4, 25 °C and 350-400 bar for 25 mM Ni(di-HCF4)₂ in D₂O/CO₂ μ Es, and 25 °C and 1 bar for 50 mM
 472 AOT in D₂O/*n*-heptane μ Es.

473

475 **Figures 5** shows changes in N_{agg} and CPP of FC6-HC n reversed micelles as a function of W_0 for
 476 FC6-HC n /D₂O/CO₂ mixtures at 45 °C and 350 bar, based on the data in **Table S2**. The figures also include
 477 data for W/CO₂ μ Es with the hybrid surfactant M-F7H4 (M=Li, K, Na) [3,33,34], double-tail surfactants
 478 n FG(EO)₂ ($n = 4$ and 8) [29], Ni(di-HCF4)₂ [21,22], and W/ n -heptane with AOT [54]. Broken circles
 479 indicate conditions at which long rod-like reversed micelles with length > 250 Å formed.

480 Similar to other reversed micellar systems of AOT, M-F7H4 and n FG(EO)₂, FC6-HC n reversed
 481 micelles also exhibited the larger N_{agg} values at higher surfactant concentrations and W_0 values. The effect
 482 of W_0 was identified as the weaker contribution as N_{agg} for FC6-HC4 doubled when W_0 increased from 25
 483 to 85. The effect of surfactant concentration is more pronounced, and N_{agg} was 74 at 17mM FC6-HC5 and
 484 $W_0=20$, but increased to 460 (i.e. 6.2 times larger) at 35 mM with almost same water content. The effects
 485 of water and surfactant concentrations on N_{agg} were based on swelling and elongating behavior of reversed
 486 micelles, respectively. The former increases μ E droplet size with increasing $A_{\text{W/C}}$, whereas the latter
 487 increases rod-like reversed micelle length without an increase in $A_{\text{W/C}}$ as the relationships between $A_{\text{W/C}}$
 488 and W_0 or surfactant concentration were clarified in supplementary data (**Figure S6**). The N_{agg} values in
 489 each n FG(EO)₂ and FC6-HC n series were similar at 17mM even if tail lengths n were different, suggesting
 490 that tail lengths of hybrid and double-tail surfactants have a small effect on N_{agg} at such a low surfactant
 491 concentration. However, the difference in N_{agg} became larger at higher surfactant concentration where
 492 morphology goes toward rod-like aggregates, even if the tail length is increased by just one methylene
 493 unit (i.e. $N_{\text{agg}} = 460$ for FC6-HC5 or 85 for FC6-HC6 at 35 mM). This would result from changes in CPP
 494 and/or hydrophilic-CO₂-philic balance (HCB) affecting differential Gibbs free energy (ΔG) [36-38,55]
 495 between the endcap and cylindrical body of rod-like reversed micelles, suggesting FC6-HC5 to have a
 496 larger ΔG (i.e. preferring the cylinder body rather than the cap).

497 From **Figure 5 (B)**, CPPs of all the surfactants were found to decrease with increasing W_0 . This
 498 decreasing CPP trend was smallest for FC6-HC4 which has the highest W_0^{max} . This may be one of the
 499 reasons for its ability to solubilizing a large amount of water, as it can keep W/CO₂ interfacial curvature

500 as negative as possible, and the W/CO_2 μE is stable against increasing W_0 . On the other hand, FC6-HC4
501 and $nFG(EO)_2$ are spherical W/CO_2 μE s and under the dilute condition they interestingly exhibited similar
502 CPP values of ~ 1.3 when W_0 reached each the maximum solubilizing power ($W_0^{\max} = 45, 62$ and 80 for
503 $4FG(EO)_2$, $8FG(EO)_2$ and FC6-HC4 respectively [25,29,35]). The CPP of ~ 1.3 is suggested to be a
504 common lowest limit to obtain spherical W/CO_2 μE s having the W_0^{\max} values. However elongated
505 micelles of M-F7H4 (M = Li and K) at near W_0^{\max} appeared with the smaller CPP of < 1.3 . Comparing
506 between AOT/W/*n*-heptane and surfactant/ W/CO_2 μE s at high surfactant concentrations ≥ 25 mM, there
507 were no significant difference in CPP. This implies no clear solvent effect between *n*-heptane and $scCO_2$
508 on CPP- W_0 (water-solubilization behaviour) for reversed-type μE s.

509 Long rod-like reversed micelles (broken circle) appeared at W_0 values of ~ 10 , surfactant
510 concentrations of ≥ 25 mM and $1.4 < CPP < 1.7$. Surfactant concentration and CPP are well-known to
511 affect reversed micelle morphology, and the appropriate values of CPP and the concentration seem
512 reasonable based on aggregation behaviour in earlier surfactant/W/O systems [56]. Even if the
513 concentration and W_0 values were appropriate for rod-like reversed micelles, surfactant/ W/CO_2 systems
514 not having the acceptable CPPs mentioned above ($1.4 < CPP < 1.7$) generated oblate ellipsoidal micelles
515 (short rods) (examples include 35 mM FC6-HC6, 78 mM Li-F7H4 [34] and 73 mM K-F7H4 [34]). The
516 appropriate W_0 values for elongated micelle formation have rarely been discussed before. The addition of
517 small amounts of water was reported to stabilise reversed micelles, and W_0 values of ~ 10 probably are
518 enough to fully conduct attractive interactions between surfactant molecules arranged side by side in
519 parallel to the rod-like reversed micelle axis. This can lower Gibbs energy of the cylindrical body
520 compared with that of the endcap [36-38,55], and then induce a long rod morphology. However,
521 increasing W_0 over 10 is likely to weaken the intermolecular attractive interactions due to the increased
522 intermolecular distance [29,35,53], and this decreases the energy difference between the endcap and body
523 of reversed micelles. This would in turn cause fragmentation of the rod-like reversed micelles.

524 Why did FC6-HC5 form the longest rod-like reversed micelles in the FC6-HC n series? This is a
525 very interesting question and finding an answer will give an important insight in developing the next-

526 generation molecular designs for CO₂-philic rod-like reversed micelles as CO₂ thickeners. **Figure S6**
527 demonstrates longer HC lengths generate larger $A_{C/W}$ resulting in smaller CPP values. This is probably
528 due to the HC-tail lying on the interface as shown in **Figure S3**, and the CO₂-phobicity and hydrophobicity
529 of HC-tails may be important feature which allows them to align on the micellar surface. Based on this,
530 FC6-HC5 is suggested to have the optimal HC length to generate appropriate CPPs of ~1.6 for the longest
531 rod-like reversed micelles. Therefore, the CO₂-phobic and hydrophobic HC-branch is identified as an
532 important feature for rod-like reversed micelle formation, in addition to both CO₂-philic tail and
533 hydrophilic groups as surfactant component parts. This is interesting new insight, since straight HC-chains
534 were previously believed to be unsuccessful for stabilizing W/CO₂ microemulsions. However, it is now
535 apparent that incorporating a HC-branch in CO₂-philic surfactant structure is a useful design feature.

536

4. Conclusions

Reversed micelles in scCO₂ can be considered VOC-free and energy-saving solvent systems for applications such as extraction, dyeing, dry cleaning, metal-plating, and organic/inorganic or nanomaterial synthesis [2]. These dispersions are even more promising, if the reversed micelles formed are rod-like assemblies, thus increasing CO₂ viscosity and significantly improving the currently poor sweep efficiency of EOR CO₂-flooding [3].

For applications such μ Es should ideally be prepared with low levels of surfactant, be inexpensive and environmentally-benign. Therefore, finding low F-content surfactants which generate a high water solubilizing power and/or form long rod-like reversed micelles is key to designing useful CO₂-philic surfactants. Previous studies [35] found hybrid surfactants HC6-HC4 and FC6-HC5 were able to generate high solubilizing power and also rod-like micelles in scCO₂, respectively. To evaluate the effectiveness of each F-atom in the solubilization the solubilizing power (i.e. W_0 value per F-atom in the molecule) is 6.2 for FC6-HC4. This is 1.5 times larger than the most effective FC-surfactant in earlier papers [10-35]. The highest effectiveness per F-atom generated by hybrid structures is also an interesting concept for designing new CO₂-philic surfactants.

To find design criteria for practical CO₂-philic surfactants having less F-atoms, this study characterised in detail nanostructures of FC6-HC_n aggregates in W/CO₂ mixtures by small-angle neutron scattering, to obtain area per headgroup, aggregation number, critical packing parameter by analysis and model fitting the SANS data. Detailed analysis about surfactant structure-aggregate morphology correlations suggested why FC6-HC4 and FC6-HC5 generated the highest solubilizing power and the longest rod-like reversed micelles in scCO₂, respectively. New findings and design criteria obtained in this study were described as followings (I)-(IV).

(I) At the dilute condition of 17mM, FC6-HC4/W/CO₂ μ Es were identified to be ellipsoidal with high W_0 values > 20. The aqueous core radii increased with W_0 as a linear function and reached 39.1 Å and 77.8

561 Å at $W_0 = 85$ (\approx the maximum solubilizing power), being the largest core in spherical W/CO₂ μ Es ever
562 reported [10-35].

563 (II) FC6-HC5 formed rod-like reversed micelles 5.3 times longer than that of FC6-HC6 under the same
564 conditions. The core length in FC6-HC5 reversed micelles was estimated as ~ 880 Å, and the length and
565 aspect ratio were identified as the longest in W/CO₂ μ Es studies. Estimated specific viscosity of the FC6-
566 HC5 rod-like reversed micelle/CO₂ solution reached 2.07 (i.e. relative viscosity = 3.07), an increase of
567 8.6 times compared to FC6-HC5 micelles. Such a high (estimated) specific viscosity for FC6-HC5 was
568 the largest viscosity enhancement of CO₂ compared to earlier surfactant/W/CO₂ systems [4-35].

569 (III) The critical packing parameter in spherical W/CO₂ μ Es decreased with water loading into the
570 reversed micelle cores, and finally reached the lowest values of ~ 1.3 (namely, the lowest limit in CPP for
571 the spherical W/CO₂ μ Es) at W_0 of each solubilizing power under the dilute surfactant condition of 17
572 mM. The decrease in CPP with increasing W_0 was the most moderate for FC6-HC4 allowing FC6-HC4
573 to achieve the highest solubilizing power.

574 (IV) Rod-like reversed micelles with lengths > 250 Å tended to appear at W_0 values of ~ 10 , surfactant
575 concentrations ≥ 25 mM and CPPs of 1.4-1.7. CPP for FC6-HC n was found to decrease with the longer
576 HC length n and the larger $A_{C/W}$. The surfactant FC6-HC5 oriented into the rod-like reversed micelle
577 formation is expected to have an optimal HC length for the appropriate CPP. Based on this consideration,
578 the CO₂-phobic and hydrophobic HC-branch was identified as an important component of the surfactant
579 to help induce rod-like reversed micelle formation.

580 As such these high water content W/CO₂ μ Es and long rod-like reversed micelles could offer a
581 new generation of universal solvents with unique properties. This study successfully identified a super-
582 efficient W/CO₂-type solubilizer FC6-HC4 and the rod-like reversed micelle-forming surfactant FC6-
583 HC5. These surfactants represent the most successful cases of low fluorine content additives and hence
584 may make further impact in this field.

585

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596

597 **Appendix A. Supplementary data**

598 Supplementary data associated with this article can be found, in the online version at.

599

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Figure captions

Figure 1. SANS profiles for FC6-HC n ($n = 4$ or 6)/D₂O/CO₂ mixtures with different W_0 values at 45 °C and 350 bar (CO₂ density = 0.92 g/cm³). Fitted curves were based on a model incorporating a Schultz distribution of polydisperse ellipsoid particles. The molar ratio of the surfactant to CO₂ was fixed at 8×10^{-4} ([Surfactant] = ~16.7 mM at the experimental conditions).

Figure 2. Changes in ellipsoidal aqueous core radii $R_{\text{ell-a}}$ and $R_{\text{ell-b}}$ for the 16.7 mM FC6-HC n /D₂O/CO₂ μ Es as a function of W_0 at 45 °C and 350 bar. The data were taken from **Table S1**. Solid and broken lines show linear functions fitted with the data for FC6-HC4 and FC6-HC6, respectively.

Figure 3. Relationship between volume-to-surface area ratio ($v_{\text{core}}/s_{\text{core}}$) of aqueous cores and W_0 for the 17mM FC6-HC n /D₂O/CO₂ μ Es at 45 °C and 350 bar. The $v_{\text{core}}/s_{\text{core}}$ values were calculated with ellipsoidal core radii listed in **Table S1**. The graph also displays data for D₂O/CO₂ μ Es with 73 mM K-F7H4, 78 mM Li-F7H4, 75-79 mM Na-F7H4, 79 mM Na-F8H4 at 23-40 °C and 380-400 bar reported in earlier papers [3,33,34].

Figure 4. SANS profiles for 35 mM and 50 mM FC6-HC n ($n = 5, 6$ or 8)/D₂O/CO₂ mixtures with $W_0 = 10$ at 45 °C and 350 bar (CO₂ density = 0.92 g/cm³). Fitted curves were based on a model incorporating a Schultz distribution of cylindrical particles (polydisperse).

752 **Figure 5.** Changes in (A) aggregation number N_{agg} of reversed micelles and (B) critical packing parameter
753 CPP as a function of W_0 for $\text{D}_2\text{O}/\text{CO}_2$ μEs with hybrid and double-tail surfactants or $\text{D}_2\text{O}/n$ -heptane μEs
754 with AOT. Experimental conditions were 45 °C and 350 bar for 17mM FC6-HC n ($n = 4$ -6) and 17mM
755 $n\text{FG}(\text{EO})_2$ ($n = 4, 8$), 23-40 °C and 380-400 bar for 78 mM Li-F7H4 and 73 mM K-F7H4, 75-79 mM Na-
756 F7H4, 25 °C and 350-400 bar for 25 mM Ni(di-HCF4) $_2$ in $\text{D}_2\text{O}/\text{CO}_2$ μEs , and 25 °C and 1 bar for 50 mM
757 AOT in $\text{D}_2\text{O}/n$ -heptane μEs .